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(54) **NANOPARTICLE COMPOSITION AND METHODS OF MAKING THE SAME**

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See application file for complete search history.

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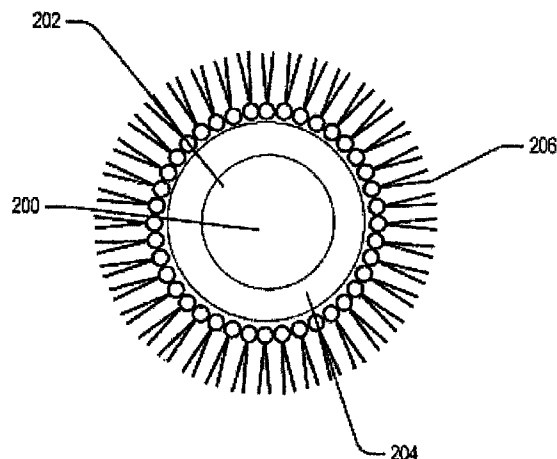
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(57) **ABSTRACT**

A method of fabricating copper nanoparticles includes heating a copper salt solution that includes a copper salt, an N,N-dialkylethylenediamine, and a C6-C18 alkylamine in an organic solvent to a temperature between about 30° C. to about 50° C.; heating a reducing agent solution that includes a reducing agent, an N,N-dialkylethylenediamine, and a C6-C18 alkylamine in an organic solvent to a temperature between about 30° C. to about 50° C.; and adding the heated copper salt solution to the heated reducing agent solution, thereby producing copper nanoparticles. A composition includes copper nanoparticles, a C6-C18 alkylamine and an N,N'-dialkylethylenediamine ligand. Such copper nanoparticles in this composition have a fusion temperature between about 100° C. to about 200° C. A surfactant system for the stabilizing copper nanoparticles includes an N,N'-dialkylethylenediamine and a C6-C18 alkylamine.

29 Claims, 4 Drawing Sheets



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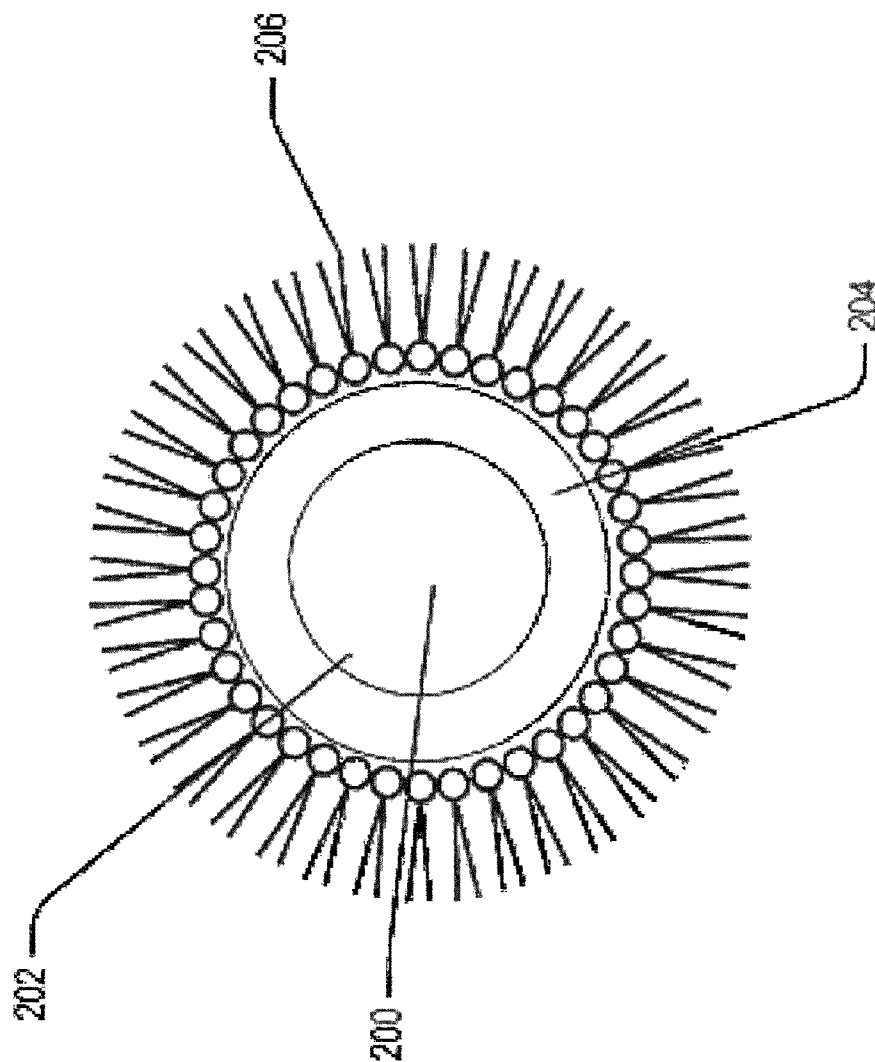


Figure 1

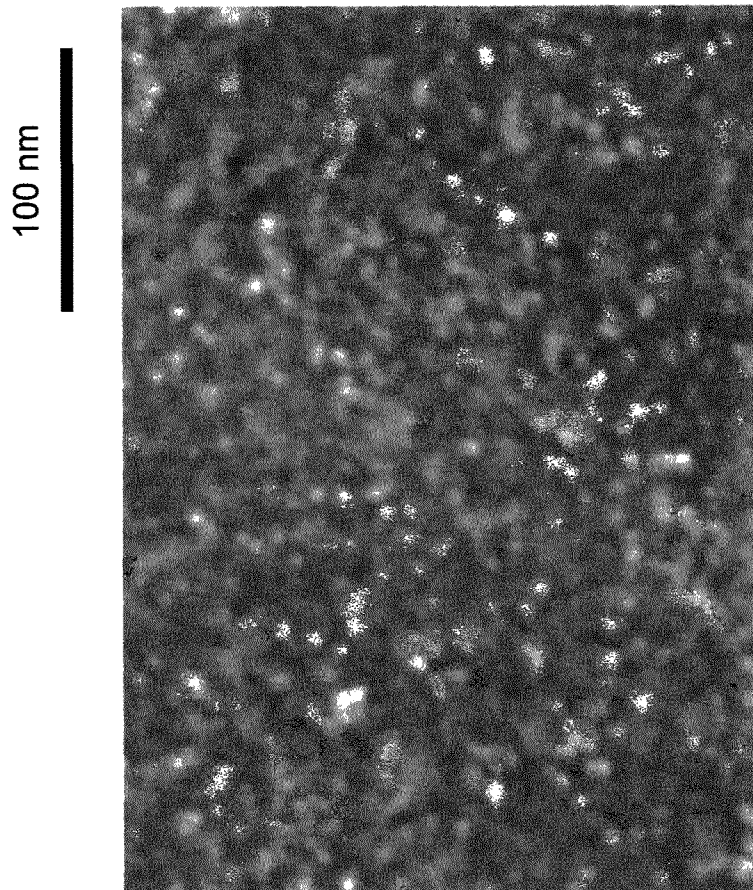


Figure 2

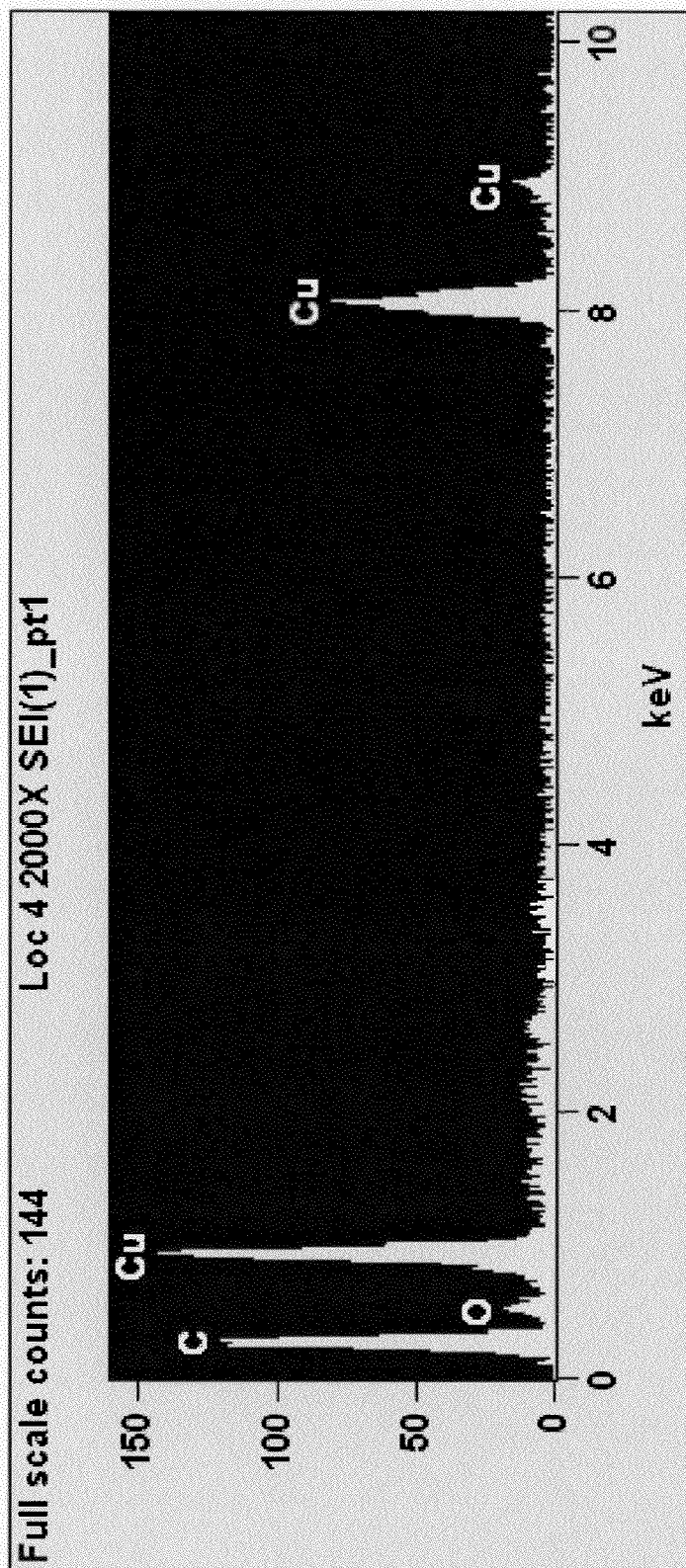


Figure 3

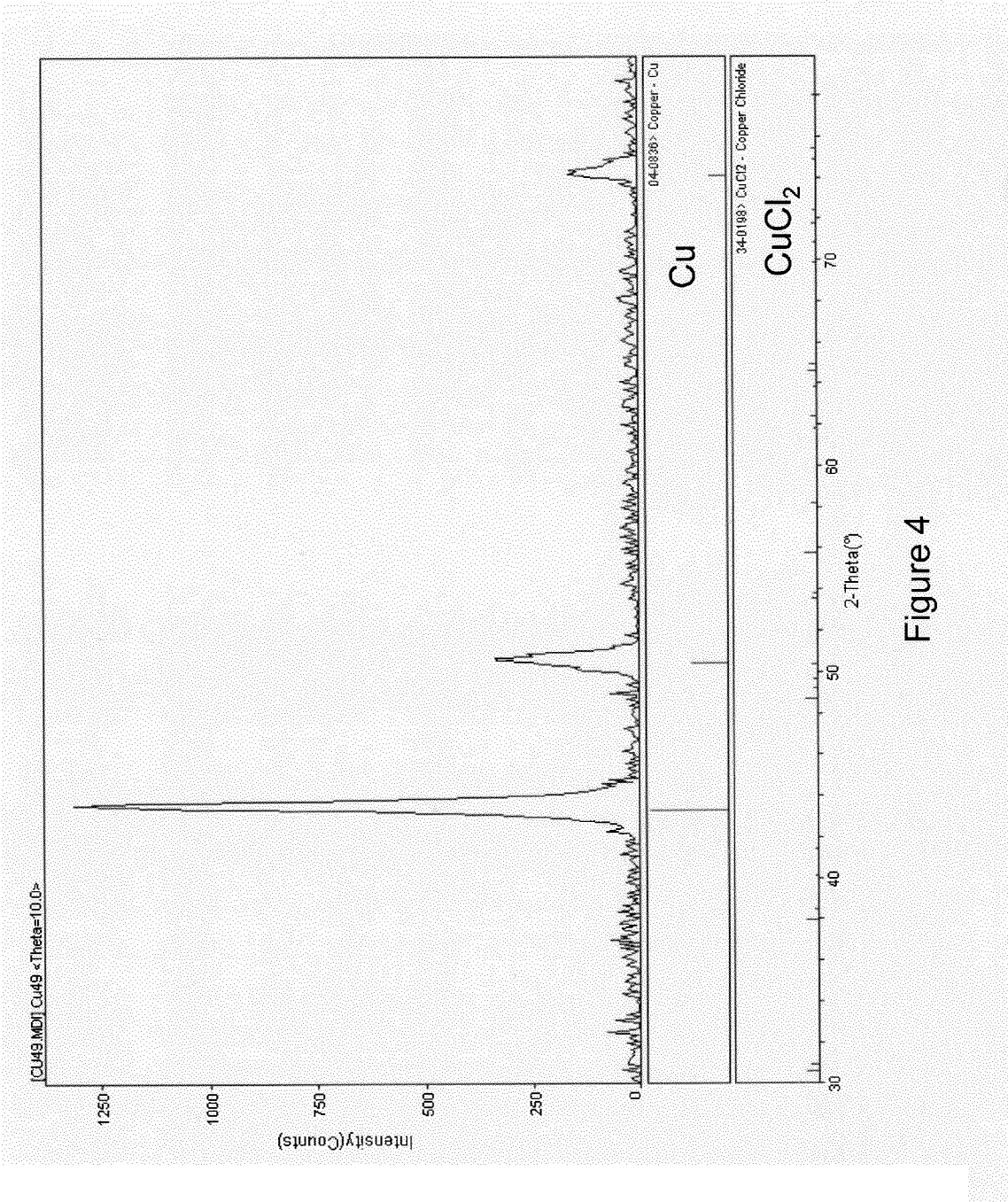


Figure 4

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NANOPARTICLE COMPOSITION AND METHODS OF MAKING THE SAME

STATEMENT OF RELATED APPLICATIONS

This application claims the benefit of priority of U.S. Provisional Application Ser. No. 61/265,326, filed Nov. 30, 2009, the entire contents of which is incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

The invention was made with Government support, and the Government has certain rights in the invention under Contract No. 700KZ8101000 awarded by SEAM.

FIELD

The present invention generally relates to nanoparticles, and more particularly to metal nanoparticles.

BACKGROUND

The formation of monodisperse copper nanoparticles remains a challenge. Chemical reduction methods in solution and in reverse micelles have provided inadequate results providing particles having irregular shapes and/or wide size distributions. A recent example utilizing a hypophosphite reducing system in the presence of polyvinylpyrrolidone (PVP) has provided monodisperse particles of relatively large sizes, between about 30-65 nm. A thermal CVD route to copper nanoparticles by decomposition of $\text{Cu}[\text{OCH}(\text{Me})\text{CH}_2\text{NMe}_2]$ has provided smaller nanoparticles on the order of 7.5 nm, but is not conducive to scale up and has not demonstrated access to even smaller particles. It would be beneficial to provide new scalable, cost-effective methods for the production of monodisperse copper nanoparticles having small effective diameters. The present invention satisfies this need and provides related advantages as well.

SUMMARY

In some aspects, embodiments disclosed herein relate to a method of fabricating copper nanoparticles that includes: heating a copper salt solution comprising a copper salt, an N,N'-dialkylethylenediamine, and a C6-C18 alkylamine in an organic solvent to a temperature between about 30° C. to about 50° C.; heating a reducing agent solution comprising a reducing agent, an N,N'-dialkylethylenediamine, and a C6-C18 alkylamine in an organic solvent to a temperature between about 30° C. to about 50° C.; and adding the heated copper salt solution to the heated reducing agent solution, thereby producing copper nanoparticles.

In some aspects, embodiments disclosed herein relate to a composition that includes copper nanoparticles, a C6-C18 alkylamine and an N,N'-dialkylethylenediamine ligand. The copper nanoparticles of the composition have a fusion temperature between about 100° C. to about 200° C.

In some aspects, embodiments disclosed herein relate to a surfactant system for the stabilizing copper nanoparticles that includes an N,N'-dialkylethylenediamine and a C6-C18 alkylamine.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows the structure of a surfactant stabilized nanoparticle of the present invention.

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FIG. 2 shows a Secondary Electron Image (SEI) of the surfactant stabilized nanoparticles of the present invention.

FIG. 3 shows the chemical analysis available via Energy Dispersive Spectroscopy (EDS) during the imaging experiment indicated in FIG. 2.

FIG. 4 shows an X-Ray Diffraction (XRD) spectrum of copper nanoparticles of the present invention.

DETAILED DESCRIPTION

Aspects disclosed herein relate to U.S. patent application Ser. No. 12/512,315, entitled "LEAD SOLDER-FREE ELECTRONICS," filed on Jul. 30, 2009. In some aspects, improvements in the synthesis of copper nanoparticles are provided, including the synthesis of copper (Cu) nanoparticles having a 3-5 nanometer (nm) size and smaller.

The present invention is directed, in part, to a method for producing monodisperse small diameter copper nanoparticles. The method employs surfactants including bidentate amines, such as N,N'-dimethyl ethylenediamine and N,N'-di-tert-butyl ethylenediamine, in the presence of medium to long chain alkylamines, under reducing conditions to provide readily scalable quantities of Cu nanoparticles (Cu NPs). Without being bound by theory, the N,N'-dialkylethylenediamines can effectively bond and stabilize the nascent Cu NPs sufficiently to produce smaller Cu NPs than those available via reducing conditions as known in the art. In some aspects, the method can provide very small Cu NPs including Cu NPs having an effective diameter of 5 nm and smaller. The methods of the invention provide fully dispersed particles that avoid agglomeration, and can also produce excellent control over particle size at below 5 nm.

Another feature of the method is the order of addition of the copper salt solution and the reducing agent solution. Reliable results are obtained by adding the copper salt solution into a reducing agent solution, as opposed to the other way around. In addition to providing small diameter Cu NPs, methods of the invention can provide nanodispersed copper(I)chloride (CuCl) that allows the controlled formation of very small nanoparticles. In some aspects, these Cu NPs produced by methods of the present invention can fuse at about 100° C. to thin copper films.

The present invention is also directed, in part, the stabilized Cu NPs made available by the methods described above. Cu NPs having diameters between 1 and 10 nm, for example, can be used as a lead free solder in electronics manufacturing. Moreover, the small diameter stabilized Cu NPs of the invention are useful in various catalytic chemical processes including the water-gas-shift reaction and in cross-coupling chemistry, such as Glaser couplings, Suzuki-Miyaura coupling of boronates and vinyl or aryl halides, the Ullmann reaction, and other copper mediated chemistry. Cu NPs of the present invention can also display unique optical and electrical properties as well.

Cu NPs of the invention can have applications in nanoelectronics and photonics materials, such as MEMS and NEMS, in biomaterials, as biomarkers, diagnostics and sensors, in nanomaterials, such as in polymers, textiles, fuel cell layers, composites and solar energy materials. Still further applications of Cu NPs of the invention include their use in antimicrobial formulations, antibiotic and antifungal agents, including their incorporation in coatings, plastics and textiles, and in copper diet supplements.

The Cu NPs of the invention are made available in scalable quantities with very small diameters in a stabilized form. Cu NPs of 5 nm or less are readily prepared, using methods of the present invention, from inexpensive copper salts and reduc-

ing agents with inexpensive solvents, under mild heating conditions, 30-50° C. By contrast, methods in the art employing Cu(acac)₂ in the presence of 1,2-hexadecanediol as a reducing agent are conducted at temperatures in excess of 150° C. in expensive octyl ether solvent. Moreover, the stabilized Cu NPs of the present invention can exhibit fusion at temperatures as low as 100° C.

As used herein, the term "copper salt" refers to any salt of copper in any of its common oxidations states, including cuprous salts, Cu(I), and cupric salts, Cu(II).

As used herein, the term "organic solvent" refers generally to polar aprotic solvents. Useful organic solvents of the invention are capable of solubilizing or acting as co-solvents to solubilize the copper salts and reducing agents.

In some embodiments, the present invention provides a method of fabricating copper nanoparticles comprising that includes 1) heating a copper salt solution that includes a copper salt, an N,N'-dialkylethylenediamine, and a C6-C18 alkylamine in an organic solvent to a temperature between about 30° C. to about 50° C.; 2) heating a reducing agent solution that includes a reducing agent, an N,N'-dialkylethylenediamine, and a C6-C18 alkylamine in an organic solvent to a temperature between about 30° C. to about 50° C.; and 3) rapidly adding the heated copper salt solution to the heated reducing agent solution, thereby producing copper nanoparticles (Cu NPs).

In carrying out methods of the invention, the heating of the substrate copper salt solution and the reducing agent solution avoids uneven temperatures on mixing and allows for rapid addition of the two solutions. It has been observed that reliable results are provided by adding the copper solution to the reducing agent rapidly, rather than adding the reducing agent solution to the copper solution. In some embodiments, rapid addition means adding the copper salt solution to the reducing agent solution in less than 5 minutes. In some embodiments, rapid addition means adding the copper salt solution to the reducing agent solution in less than 4 minutes, in less than 3 minutes in other embodiments, in less than 2 minutes in still further embodiments, and in less than 1 minute in yet still further embodiments.

In some embodiments, the Cu NPs formed by methods of the present invention can be used in situ without further isolation. In other embodiments, a work up of the reaction can be performed to purify and isolate the CuNPs. Such purification can include a series of rinses, sonication, and centrifugation steps as described in Example I below.

In some embodiments, the copper salt used in methods of the present invention is selected from a copper halide, copper nitrate, copper acetate, copper sulfate, copper formate, and copper oxide. Other copper (I) or copper (II) salts can be used as well. One skilled in the art will recognize the benefit of choosing a copper salt having good solubility in the organic solvent being employed. Moreover, the choice of copper salt can be a function of cost and scale. Methods of the present invention when conducted on large scale benefit can use inexpensive copper halide salts, for example. In some embodiments, the copper salt is a copper halide selected from copper chloride, copper bromide, and copper iodide. In particular embodiments, the copper salt is copper chloride.

In some embodiments, methods of the present invention are carried out in an organic solvent. The organic solvent can be anhydrous in some embodiments. The organic solvent can be any polar aprotic capable of at least partially solubilizing the copper salt and reducing agent. In some embodiments, the organic solvent is triglyme which dissolves the copper chloride precursor effectively while also activating the reducing agent sodium borohydride (NaBH₄). By contrast, simple

ethers, like diethyl ether, do not readily dissolve such a reducing agent. The organic solvent need not on its own dissolve the copper salt. In some embodiments, the presence of the N,N'-dialkylethylenediamine, the C6-C18 alkylamine, or both in combination can enhance the solubility of the copper salt through the formation of copper-organic ligand complex.

In some embodiments, methods of the present invention employ an N,N'-dialkylethylenediamine which includes a C1-C4 N,N'-dialkylethylenediamine. As bidentate ligands, N,N'-dialkylethylenediamines can coordinate metal atoms at two nitrogen atoms, which can stabilize the formation of small diameter Cu NPs. In some embodiments, the alkyl groups of the C1-C4 N,N'-dialkylethylenediamine are the same, while in other embodiments they are different. The C1-C4 alkyl groups include methyl, ethyl, propyl, butyl, and the like, including normal chain or branched alkyl groups such as iso-propyl, iso-butyl, sec-butyl, and tert-butyl groups. Other bidentate, tridentate, and multidentate ligands can also be employed. For example, N,N'-dialkylpropylenediamines can also be used.

The amount of N,N'-dialkylpropylenediamine employed in the reaction is in a range from between about 12 percent to about 16 percent by volume based on the total reaction mixture after addition of the solution containing the reducing agent.

In some embodiments, methods of the invention use C6-C18 alkylamines. In some embodiments the alkylamine employed is a C7-C10 alkylamine. Although a C5 or C6 alkylamine can also be used. Likewise, a C11 or C12 alkylamine can also be used. The exact size of alkylamine to be employed can be a balance between being long enough to provide an effective inverse micellar structure versus the ready volatility and/or ease of handling. For example, alkylamines with more than 18 carbons while also usable, can be more difficult to handle because of their waxy character. Alkylamines between C7 and C10, inclusive, represent a good balance of desired properties for ease of use. In some embodiments, the C6-C18 alkylamine is n-heptylamine. In some embodiments, the C6-C18 alkylamine is n-octylamine. In some embodiments the C6-C18 alkylamine is n-nonylamine. While these are all normal chain amines, one skilled in the art will appreciate that some extent of branching can also be used. For example, 7-methyloctylamine can also be used. Without being bound by theory, the monoalkylamines described above can also serve as ligands in the coordination sphere of copper atoms. However, their ability to dissociate from the copper center is facilitated by the single point of attachment.

The amount of C6-C18 alkylamine employed in the reaction is in a range from between about 10 to about 15% based on the total reaction mixture after addition of the solution containing the reducing agent. Moreover, the ratio of the N,N'-dialkylpropylenediamine to C6-C18 alkylamine can be in a range from between about 1:1 to about 2:1.

In some embodiments, the methods of the invention also include a solution of a reducing agent. The reduction of copper salts by a variety of reducing agents are known in the art. A reducing agent can be chosen that will reduce copper (II) to copper (0), copper (I), or mixtures thereof. One skilled in the art will recognize that when employing a hydride based reducing agent, the hydride source will provide the requisite change in copper oxidation state and avoid the formation of copper hydride species. In some embodiments, the reducing agent is a hydride-based reagent such as sodium borohydride.

In some embodiments, methods of the invention produce copper nanoparticles in a range of sizes from between about 1 nm to about 10 nm when the temperature used to mix the

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solution of copper salt and reducing agent are in a range between about 30° C. to about 50° C. The size of the Cu NPs formed is sensitive to temperature. For example, when heating of the solution of copper salt and solution of reducing agent is in a range from between about 30° C. to about 45° C., the resultant copper nanoparticles range in size from between about 1 nm to about 5 nm. Similarly, when heating copper salt and reducing agent solutions in a range from between about 45° C. to about 50° C., the resultant copper nanoparticles range in size from between about 5 nm to about 10 nm. The control of the temperature over this narrow range is facilitated by the separate heating of the copper salt solution and reducing agent solution prior to mixing.

In some embodiments, the present invention provides a stabilized copper nanoparticle made by the methods described herein above. Such Cu NPs can range in size from between about 1 nm to about 10 nm. Without being bound by theory, the CuNPs are stabilized by the presence of the C6-C18 alkylamine or N,N'-dialkylethylenediamine, or the combination of the two. The association of these ligands are shown in FIG. 1. The nanoparticle **200** shown in FIG. 1 includes a dense core **202**, a lower density shell **204**, with indications of a smooth transition between the two. Finally, the protected nanoparticle include a protective surfactant layer **206**. The procedure for generating nanoparticles of the invention are described further below in the Example.

In some embodiments, the stabilized Cu NPs range in size from about 1 nm to about 10 nm. In other embodiments, the stabilized Cu NPs range in size from between about 1 nm to about 5 nm. In still further embodiments, the Cu NPs range in size from between about 2 nm to about 5 nm. In yet still further embodiments, the Cu NPs range in size from between about 3 nm to about 5 nm. In yet other embodiments, the Cu NPs range in size from between about 5 nm to about 10 nm. The Cu NPs of the invention are monodisperse and generally spherical in geometry, see Example below.

Based on the methods described herein above, the present invention provides a composition that includes copper nanoparticles, a C6-C18 alkylamine and an N,N'-dialkylethylenediamine ligand. These copper nanoparticles are stabilized and are useful in a variety of applications. As described above the C6-C18 alkylamine can play a role in the stabilization of the Cu NPs. In particular embodiments, the C6-C18 alkylamine used to stabilize the Cu NPs is a C7-C10 alkylamine, such as n-heptylamine, n-octylamine, n-nonylamine, or n-decylamine. In exemplary embodiments, the N,N'-dialkylethylenediamine is N,N'-dimethylethylenediamine or N,N'-di-tert-butylethylenediamine. In some embodiments, the Cu NPs of the invention can have a fusion temperature between about 100° C. to about 200° C., providing a material that can be used as a low melt solder. One skilled in the art will recognize the size dependence on the observed fusion temperature. Thus, smaller Cu NPs of the invention display lower fusion temperatures.

The low fusion temperatures of the Cu NPs of the invention provide a lead-free solder for electronics applications. Similar approaches use silver and gold ink with a fusion temperature of about 200° C. (e.g. NanoMas Inc.) and even above 300° C. (Virginia Institute of Technology) at a cost of about \$1,000 per gram. Cu NPs of the invention provide a substantial cost reduction over these approaches. The process to make the Cu NPs described herein is readily scalable and allows low cost mass production. In some embodiments, the Cu NPs of the invention are used in a formulation of ink for ink jet printing of conducting vias. This can be useful in the production of a low cost flexible thin film solar cell, for example.

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In some embodiments, the present invention provides a surfactant system for the stabilizing copper nanoparticles comprising an N,N'-dialkylethylenediamine and a C6-C18 alkylamine. In some such embodiments, the N,N'-dialkylethylenediamine and a C6-C18 alkylamine are present in a ratio from between about 1:1 to about 2:1. One skilled in the art will recognize that the dual surfactant system having the bidentate N,N'-dialkylethylenediamine and a C6-C18 alkylamine can be used in conjunction with the preparation of other metal nanoparticles. For example, this surfactant system can be used to generate NPs of silver, gold, rhodium, rhenium, nickel, palladium, platinum, and other transition metals, or transition metal oxides, and other salts.

It is understood that modifications which do not substantially affect the activity of the various embodiments of this invention are also included within the definition of the invention provided herein. Accordingly, the following example is intended to illustrate but not limit the present invention.

Example 1

This Example shows an exemplary preparation and characterization of Cu Nps, in accordance with some embodiments of the invention.

0.8 g of copper (II) chloride dihydrate were placed into a 250 mL 3 neck round bottom flask, evacuated and back-filled with Argon three times. A plastic syringe and a stainless steel needle was used to add the following surfactants in the order given and under positive Argon pressure: 4 mL of N,N'-di-tert-butylethylenediamine, 4 mL n-nonylamine and 45 mL degassed triglyme as the reaction medium. The color of the solution turned dark blue and was stirred and heated for 2 hours at 45° C.

A second 250 mL 3 neck round bottom flask was charged with 8 mL of dry 2.0 M sodium borohydride solution. A plastic syringe and a stainless steel needle was used to add the following surfactants in the order given and under positive Argon pressure: 4 mL of nonylamine and 6 mL of N,N'-di-tert-butylethylenediamine. The resulting solution was colorless, and was heated to 45° C. and stirred for 1 hour; when heat was applied to this solution, it turned slightly cloudy.

While keeping both flasks at 40° C., the copper (II) chloride solution was transferred to the flask containing sodium borohydride over a period of five minutes using a cannula. When transfer was complete the reaction looked dark purple. In 10 minutes, the mixture turned cloudy and stayed white for about 4 minutes. Subsequently, the reaction kept changing color from white, to yellow-brown and eventually became dark brown over the next five minutes. At this point, it was cooled down to -10° C. in a dry ice and acetone bath for 10 minutes.

The reaction mixture was centrifuged at 1000 RPM for 20 minutes, which resulted in a dark brown precipitate and a clear supernatant. The black precipitate was mixed with a solution of degassed hexane (80 mL) and dicyclohexylamine (10 mL), which was then sonicated for 10 minutes. The new mixture was centrifuged at 1000 RPM for 10 minutes, a black precipitate and clear supernatant was obtained. The black precipitate was mixed with a solution of degassed toluene (80 mL) and dicyclohexylamine (10 mL), which was then sonicated and centrifuged at 1000 RPM for 10 minutes. A black precipitate and a clear supernatant were obtained. In the next step, 40 mL of degassed DI water was added to the black precipitate as well as 40 mL toluene and 5 mL dicyclohexylamine. The mixture was shaken and sonicated for 10 minutes to mix and disperse everything. The addition of the DI water caused some gas evolution and bubbling. Then, the mixture was sonicated and centrifuged at 1000 RPM for 20 minutes,

which resulted in 3 layers: a dark brown organic (top layer), a second slightly cloudy aqueous layer (middle layer) and a small amount of a dark brown/copper color precipitate (bottom layer). The organic layer as well as the precipitate were isolated and stored in a glass vial under Argon and kept in a freezer at -5°C .

Scanning Electron Microscope Analysis:

A JEOL JSM7001-FLV Scanning Electron Microscope (SEM) was employed in this analysis. In addition to Secondary, Backscattering and Low Vacuum Imaging, this SEM has a Scanning Transmission Electron Detector (STEM) that produces an image similar to that of a Transmission Electron Microscope (TEM). The SEI image is shown in FIG. 2. Samples were prepared using a dilute organic solution and TEM grids (Cu/Au, carbon coated, 200/300 grid), the specified resolution was 1.2 nm at 30 kV and 3 nm at 1 kV. The magnification range was from $20\times$ to $1,000,000\times$. The SEM also offers quick chemical analysis using Energy Dispersive Spectroscopy (EDS). The EDS in FIG. 3 shows the copper and carbon from the surfactant shell. The EDS indicates a small quantity of oxygen due to surfactant removal in the vacuum chamber and some oxidation from oxygen back pressure during pump down in collecting the SEM.

SEM Sample Preparation:

The organic layer obtained from Reaction Cu53 was used to prepare the Scanning Electron Microscope (SEM) samples. In this particular case, lacey carbon film on 300 mesh gold grid was used for preparation of the SEM sample. A 2 mL glass pipette was used to place 3 drops of the organic solution on the gold grid which was dried in air under the hood.

X-Ray Diffraction Analysis:

A Siemens D5000 Diffraktometer. Sample preparation: The dark precipitate obtained from reaction Cu53 was isolated and dried in air on a watch glass. A double sided sticky tape (0.5 cm $\times$ 1 cm) was placed in the center of a standard glass slide. The dark powder was placed on the tape and pressed down for good adhesion such that it covers the entire tape. The glass slide was placed in the XRD sample holder and the run conducted using the following conditions: Range 30° - 80° , Step size: 0.1, Dwell time: 12, Deg: 5, Theta: 10° , Laser Voltage (kV) 40 and Current (mA) 30, run time 96 minutes. The XRD spectrum, shown in FIG. 4, indicates the presence of copper metal only, with no precursor copper salt or oxide detected.

A reference to an element in the singular is not intended to mean "one and only one" unless specifically stated, but rather "one or more." The term "some" refers to one or more. Underlined and/or italicized headings and subheadings are used for convenience only, do not limit the invention, and are not referred to in connection with the interpretation of the description of the invention. All structural and functional equivalents to the elements of the various embodiments described throughout this disclosure that are known or later come to be known to those of ordinary skill in the art are expressly incorporated herein by reference and intended to be encompassed by the invention. Moreover, nothing disclosed herein is intended to be dedicated to the public regardless of whether such disclosure is explicitly recited in the above description.

What is claimed is:

1. A method of fabricating copper nanoparticles comprising:

heating a copper salt solution comprising a copper salt, an N,N' -dialkylethylenediamine, and a C6-C18 alkylamine in an organic solvent to a temperature between about 30°C . to about 50°C .;

heating a reducing agent solution comprising a reducing agent, an N,N' -dialkylethylenediamine, and a C6-C18 alkylamine in an organic solvent to a temperature between about 30°C . to about 50°C .; and

adding the heated copper salt solution to the heated reducing agent solution, thereby producing copper nanoparticles.

2. The method of claim 1, wherein the copper salt is selected from a copper halide, copper nitrate, copper acetate, copper sulfate, copper formate, and copper oxide.

3. The method of claim 2, wherein the copper halide is selected from copper chloride, copper bromide, and copper iodide.

4. The method of claim 3, wherein the copper halide is copper chloride.

5. The method of claim 1, wherein the organic solvent is triglyme.

6. The method of claim 1, wherein said N,N' -dialkylethylenediamine comprises a C1-C4 N,N' -dialkylethylenediamine.

7. The method of claim 1, wherein the C6-C18 alkylamine is a C7-C10 alkylamine.

8. The method of claim 1, wherein the C6-C18 alkylamine is n -heptylamine.

9. The method of claim 1, wherein the C6-C18 alkylamine is n -octylamine.

10. The method of claim 1, wherein the C6-C18 alkylamine is n -nonylamine.

11. The method of claim 1, wherein the reducing agent is sodium borohydride.

12. The method of claim 1, wherein the produced copper nanoparticles range in size from between about 1 nm to about 10 nm.

13. The method of claim 1, wherein the heating of the solution of copper salt and the solution of reducing agent is in a range from between about 30°C . to about 45°C .

14. The method of claim 13, wherein the produced copper nanoparticles range in size from between about 1 nm to about 5 nm.

15. The method of claim 1, wherein the heating of the solution of copper salt and the solution of reducing agent is in a range from between about 45°C . to about 50°C .

16. The method of claim 15, the produced copper nanoparticles range in size from between about 5 nm to about 10 nm.

17. The method of claim 1, wherein the addition step is performed in less than 5 minutes.

18. The method of claim 1, wherein the addition step is performed in less than 4 minutes.

19. The method of claim 1, wherein the addition step is performed in less than 3 minutes.

20. The method of claim 1, wherein the addition step is performed in less than 2 minutes.

21. The method of claim 1, wherein the addition step is performed in less than 1 minute.

22. A stabilized copper nanoparticle made by a method comprising:

heating a copper salt solution comprising a copper salt, an N,N' -dialkylethylenediamine, and a C6-C18 alkylamine in an organic solvent to a temperature between about 30°C . to about 50°C .;

heating a reducing agent solution comprising a reducing agent, an N,N' -dialkylethylenediamine, and a C6-C18 alkylamine in an organic solvent to a temperature between about 30°C . to about 50°C .; and

adding the heated copper salt solution to the heated reducing agent solution, thereby producing copper nanoparticles.

23. A composition comprising copper nanoparticles, a C6-C18 alkylamine and an N,N'-dialkylethylenediamine ligand, said copper nanoparticles of said composition having a fusion temperature between about 100° C. to about 200° C.

24. The composition of claim **23**, wherein the C6-C18 5
alkylamine is a C7-C10 alkylamine.

25. The composition of claim **23**, wherein the C6-C18
alkylamine is n-heptylamine.

26. The composition of claim **23**, wherein the C6-C18
alkylamine is n-octylamine. 10

27. The composition of claim **23**, wherein the C6-C18
alkylamine is n-nonylamine.

28. The composition of claim **23**, wherein the copper nano-
particles range in size from between about 1 nm to about 10
nm. 15

29. The composition of claim **23**, wherein the copper nano-
particles range in size from between about 1 nm to about 5
nm.

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